SUBSTRATE PROCESSING METHOD AND INK JET RECORDING HEAD SUBSTRATE MANUFACTURING METHOD

FIELD OF THE INVENTION AND RELATED ART

The present invention relates to a method for processing a substrate and a method for manufacturing a substrate for an ink jet recording head.

An ink jet printing system is negligibly small in the noises which occur during a printing operation, and is capable of printing at a high speed. In addition, it is capable of printing on the so-called plain paper, that is, without the need for giving the plain paper a special treatment. Therefore, an ink jet printing system has come to be widely used in recent years.

There are various ink jet recording heads usable with an ink jet recording system. Among these ink jet recording head, an ink jet recording head of the so-called side shooter type has been well-known, which ejects droplets of liquid, for example, liquid ink, in the direction perpendicular to the surface of the substrate of the ink jet recording head, on which the energy generation elements for generating the energy used for ejecting the ink were formed.

Japanese Laid-open Patent Application 6-286149 discloses one of the methods for manufacturing a side shooter ink jet recording head. According to

this method, liquid path walls and liquid ejection orifices are formed by forming an ink path mold of dissolvable resin, on an ink jet recording head substrate, coating the liquid path mold with resin, the main ingredient of which is epoxy, and pattering the resin.

Generally, a side shooter head structured so that its ink supply hole for providing the ink paths, in which the energy generation elements are disposed, penetrates from one surface of the substrate, which supports the energy generation elements, to the other. One of the methods for forming this ink supply hole is an anisotropic etching method. When a silicon substrate (wafer), the crystal orientation planes of which are (100) and (110), is chemically etched with the use of alkaline solution from the directions of the planes (100) and (110), the rate at which the etching process progresses against the plane (111) is extremely small relative to the rates at which the etching process progresses against other planes. In other words, the rate at which the silicon substrate is etched is affected by the crystal orientation of the silicon substrate. That is, the rate at which the silicon substrate is etched in the depth direction of the ink supply hole, or the thickness direction of the substrate, becomes different from the rate at which the substrate is etched in the width direction of the

ink supply hole.

For example, when a silicon substrate having the crystal orientation plane of (100) is etched from the direction of the plane (100), the depth to which the substrate is etched is determined by the width by which the substrate is etched. Therefore, the width of the ink supply hole, on the side from which the etching is started, can be controlled by controlling the width of the surface area of the substrate, across which the etching is started. More specifically, a hole (ink supply hole), the internal surface of which is tilted at 54.7° so that the cross section of the hole, parallel to the surfaces of the substrate, gradually reduces from the substrate surface, from which the etching is started, toward the surface opposite thereto. In other words, the width of the ink supply hole, on the side from which the etching is to be started, and the width of the ink supply hole, on the side opposite therefrom, can be easily controlled by taking into consideration, the thickness of the substrate and the width by which the substrate is etched.

Generally, in a chemical etching method such as the above described one in which alkaline solution is used, an object to be etched is etched for a relatively long time with the use of strong alkaline solution, and also, the solution is heated.

Therefore, dielectric film such as silicon oxide film has been used as the material for an etching mask.

Japanese Laid-open Patent Application 2001-10070 proposes a method for making it difficult for pinholes from growing through a mask during an anisotropic etching operation. According to this method, polyether amide film is used as the material for a mask for pattering the silicon oxide film is used, and hydrofluoric acid, or mixed solution of hydrofluoric acid and ammonium fluoride, is used as etching liquid. Further, two films, that is, silicon oxide film and polyether amide film, are used as the materials for masks used for anisotropically etching a silicon substrate.

Japanese Laid-open Patent Application discloses another substrate processing method. According to this method, polyether amide film is formed as the layer for sealing between a nozzle formation member and a substrate. More specifically, polyether amide is solvent coated, and the solvent is evaporated by heating the coat at a temperature no less than the glass transition point (230°C) of polyether amide in order to reduce the internal stress of the polyether amide layer, since the polyether amide is thermoplastic.

However, when forming the ink supply hole through a silicon substrate with the use of an

anisotropic etching method, not only etching progresses in the depth direction of the ink supply hole, which is equivalent to the thickness direction of the substrate, but also in the direction perpendicular to the thickness direction of the substrate, or the width direction of the hole (which hereinafter will be referred to "side etching"). Therefore, the silicon oxide film which functions as a mask for protecting silicon as the material for the substrate will be left partially projecting into the ink supply hole after the formation of the hole. This portion of the silicon oxide film projecting into the ink supply hole is possible to break off and turn into debris, during the subsequent ink jet recording head manufacturing steps, for example, while an ink jet recording head is assembled, while an ink jet recording head is packaged, and also, while an ink jet recording head is used.

As the solutions to the above described problems, Japanese Laid-open Patent Application 11-010895 proposes a substrate processing method, according to which only the portion of the silicon oxide film projecting into the ink supply hole is removed, while leaving intact the portion of the silicon oxide film covering the reverse surface of the substrate, by etching the silicon oxide film for a proper (precise) length of time, with the use of

hydrofluoric acid, or the mix solution of hydrofluoric acid and ammonium fluoride. However, this method is also problematic in that it is very difficult to properly control the length of etching time.

The present invention was made in consideration of the above described problems, and its primary object is to provide an ink jet recording head substrate, in which the substrate surface, on the side from which the ink supply hole is formed, is precisely covered with protective film, to the very edge of the hole. Another object of the present invention is to provide an ink jet recording head substrate processing method, the use of which for manufacturing an ink jet recording head substrate can reduce the ratio at which defective ink jet recording heads are manufactured, in order to provide an ink jet recording head capable of forming a high quality image, and to reduce ink jet recording head cost.

SUMMARY OF THE INVENTION

The present invention relates to a substrate processing method characterized in that it comprises: a step for forming a protective film on the substrate; a step for etching the surface of the protective film; a step for forming etchant-resistant film on the etched surface of the protective film; a step for forming an ink supply hole pattern through the

etchant-resistant film and protective film; a step for forming the ink supply hole through the substrate by etching; a step for removing the portion of the protective film left projecting into the ink supply hole while forming the hole; and a step for removing the etchant-resistant film.

The present invention relates to a manufacturing method for an ink jet recording head substrate, in which the hole for supplying liquid is formed in a manner of penetrating the substrate, and on which the energy generation elements for generating the energy for ejecting liquid are disposed, characterized in that it comprises: a step for forming a protective film on the surface of the substrate opposite to the surface on which the energy generation elements are present; a step for etching the surface of the protective film; a step for forming etchant-resistant film on the etched surface of the protective film; a step for forming an ink supply hole pattern through the etchant-resistant film and protective film; a step for forming the ink supply hole through the substrate by etching through the ink supply hole pattern; a step for removing the portion of the protective film left projecting into the ink supply hole while forming the hole; and a step for removing the etchant-resistant film.

With the application of the present

invention, it becomes possible to provide an ink jet recording head substrate, the surface which on the side from which the ink supply hole is formed is precisely covered with a protective film. Further, manufacturing an ink jet recording head with the use of an ink jet recording head substrate manufactured with the use of the substrate processing method in accordance with the present invention makes it possible to raise the level of tightness between the protective film and the etchant-resistant film, preventing thereby the etchant-resistant film from exfoliating or floating from the protective film. Therefore, it becomes easier to control the process for removing the portion of the protective film projecting into the ink supply hole.

Also with the application of the prevent invention, not only can the etchant-resistant film be made to better function as the etching mask for the protective film, but also the protective film can be made to better function as the etching mask for the substrate. Further, the etchant-resistant film can be made to better function as the protective film for the reverse surface of the substrate. As a result, it is possible to reduce the ratio at which defective ink jet recording heads are manufactured, making it possible to manufacture an ink jet recording head capable of forming a high quality image, and to reduce

head cost.

These and other objects, features, and advantages of the present invention will become more apparent upon consideration of the following description of the preferred embodiments of the present invention, taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic drawing showing the method, in accordance with the present invention, for manufacturing an ink jet recording head substrate.

Figure 2 is a schematic drawing showing the method, in the first embodiment of the present invention, for manufacturing an ink jet recording head.

Figure 3 is a schematic drawing showing Comparative Method 1 for manufacturing an ink jet recording head substrate.

Figure 4 is a photograph of the reverse side of an ink jet recording head manufactured using the ink jet recording head manufacturing method in the first embodiment of the present invention.

Figure 5 is a photograph of the reverse side of the ink jet recording head manufactured using the comparative ink jet recording head manufacturing method.

Figure 6 is a schematic drawing showing the positioning of a wafer in the etching bath, in the ink jet recording head substrate processing method in the first embodiment and the comparative method.

Figure 7 is a schematic drawing showing the directions in which the etching fluid flows toward, or away from, the wafer in the etching bath shown in Figure 6.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is applicable not only to an ink jet recording apparatus, or a recording apparatus which uses ink, but also to an apparatus for ejecting various liquids onto specific points of various surfaces. Hereinafter, however, the present invention will be described with reference to an apparatus which ejects ink.

As an energy generation element, an electrothermal transducer element or an piezoelectric element is usable. When using an electrothermal transducer element as an energy generation element, ink is given thermal energy from the electrothermal transducer element in order to generate bubbles in the ink, and ink is ejected by the pressure from the bubbles. When using a piezoelectric element as an energy generation element, ink is ejected by the mechanical energy from the piezoelectric element.

Processing a substrate with the use of one of the methods in accordance with the present invention for processing a substrate makes it possible to raise the level of tightness with which silicon oxide film as protective film and the polyether amide film as etchant-resistant film formed on the protective film are adhered to each other, in order to prevent etchant-resistant film from exfoliating and/or floating from the protective film, during various manufacturing steps. Therefore, such a substrate processing method makes it easier to control the step in which the portion of silicon oxide film as protective film left projecting into the ink supply hole after the formation of the hole. Also, it makes it possible to make the etchant-resistant film better function as the mask for etching the protective film, and also, the protective film to better function as the mask for etching the substrate. Further, it makes the etchant-resistant film better function as the protective film for the reverse surface of the substrate.

When a multipurpose semiconductor manufacturing apparatus is used to manufacture an ink jet recording head having energy generation elements, driving circuits therefor, and the like, foreign substances sometimes adhere to the protective film on the reverse surface of a substrate, while the

substrate is conveyed from the apparatus for performing one manufacturing step to the apparatus for performing another manufacturing step. If etchant-resistant film is formed on an area of protective film, across which foreign substances have adhered, the etchant-resistant film sometimes exfoliates and/or floats from the protective film, starting from where the foreign substances are present. The process in accordance with the present invention for cleaning a protective film is extremely effective to clean the surface of the protective film, that is, to remove the foreign substances on the protective film, which possibly will trigger the exfoliation and/or floating of the etchant-resistant film from the protective film.

Further, the removal of the foreign substances on the surface of the protective film reduces the overall thickness of the protective film, reducing thereby the time required to etch the protective film, with the presence of the etchant-resistant film thereon, and the time required to remove the protective film. Therefore, it reduces the length of time the etchant-resistant film is subjected to these processes, reducing thereby the possibility that the etchant-resistant film will exfoliate and/or float. As a means for preventing the etchant-resistant film from exfoliating and/or floating, it is

also possible to use a substrate which is thinner, but not thin enough to be substantially lower in strength and break in a manufacturing step, or to make a substrate thinner by polishing the substrate, or etching the substrate with the use of acid, before forming the protective film on the reverse surface of the substrate. These means can also reduce the time necessary to form the ink supply hole by etching, reducing thereby the length of time the etchant-resistant film is exposed to alkaline etching liquid.

Hereinafter, the steps in the preferred method in accordance with the present invention for processing a substrate in order to manufacture an ink jet recording substrate will be described with reference to the appended drawings.

Figure 1 is a schematic drawing showing the method in accordance with the present invention for manufacturing an ink jet recording head substrate. Figure 1(a) shows a step (a) in which silicon oxide film 103 as a protective film is formed on the reverse surface of a substrate 101 formed of silicon crystal, that is, the surface of the substrate 101, across which the energy generation elements 102 are not present. In order to make it possible to anisotropically etch the substrate 101, a wafer formed of a silicon crystal, the crystallographic planes of which are (100) and (110), and the front and

reverse surfaces of which are parallel to the crystallographic planes of the silicon crystal, is used as the substrate 101. The thickness of the substrate 101 is chosen in consideration of the strength required of the substrate for an ink jet recording head, etching rate in an anisotropic etching, which will be described later, etc. The silicon oxide film as a protective film is desired to be formed with the use of a thermally oxidizing method, which yields silicon oxide film of good quality. However, it may be formed with the use of CVD, sputtering, or the like.

Figure 1(b) shows a step (b) in which the surface of the silicon oxide film is cleaned by etching. In this step, the value to which the thickness of the silicon oxide film is to be set so that the cleaned silicon oxide film will properly function as the etchant-resistant film for protecting the reverse surface of the substrate 101 during the anisotropic etching process, which will be described later. It is no more than 1,000 nm, preferably, no more than 500 nm. As the foreign substances having adhered to the surface of the silicon oxide film during the formation thereof are removed by etching the surface of the silicon oxide film, not only does the silicon oxide film become uniform in quality, but also, it is improved in surface properties. Etching

is more effective to clean the silicon oxide film than cleaning it with surfactant.

Next, in the step (c) shown in Figure 11(c), etchant-resistant film for protecting the silicon oxide film is formed on the cleaned surface of the silicon oxide film. As a material for this etchant-resistant film, polyether amide resin or the like are usable, which is excellent in terms of the resistance to the etching liquid for etching the silicon oxide film and the etching liquid for forming a liquid (ink) supply hole, and also, are excellent in terms of adhesiveness to the silicon oxide film. The film formed of polyether amide resin functions as a very effective etching mask when etching with the use of hydrofluoric acid, mixture of hydrofluoric acid and ammonium fluoride, or the like. When polyether amide resin is used as the material for the etchant-resistant film, it is solvent coated with the use of appropriate solvent, and the solvent is evaporated by heating the coated mixture of polyether amide and the solvent to a temperature in the range of 60°C - 350°C, preferably, 320°C - 350°C, in order to form polyether amid film on the surface of the silicon oxide film. The coating method which uses solvent makes it possible to simply and evenly coat polyether amide resin in liquid form. The temperature to which the mixture of the polyether amide resin and the solvent

is to be heated to form the polyether amide film is desired to be no less than 230°C which is the glass transition point of polyether amide resin, and no more than 400°C at (above) which polyether amide resin will crack. As polyether amide resin, HIMAL HL-1200 (Hitachi Chemical Co., Ltd.), for example, can be used.

Next, the patterning for forming a hole corresponding to the liquid (ink) supply hole, through the etchant-resistant film is carried out. The method for this pattering is optional; it can be selected in accordance with the material for the etchant-resistant film. If polyether amide resin film is formed as the material for the etchant-resistant film, the hole is desired to be formed using the following process. That is, photosensitive resin is coated on the polyether amide film, and the coated surface is exposed to a predetermined pattern. Then, the photosensitive sin is developed to yield the photosensitive resin film having the predetermined pattern. The polyether amide film is etched using, as a mask, this photosensitive resin film having the predetermined pattern. Then, the photosensitive resin is removed.

One of the important points in the present invention is in which step of the ink jet recording head manufacturing process to form the polyether amide

resin film. During the formation of the polyether amide film, the mixture of polyether amide resin and solvent is heated at a temperature no lower than the glass transition point of polyether amide resin, in order to minimize the amount by which stress is generated in the polyether amide resin during the formation thereof, as described above. This heating process is desired to be carried out immediately after the coating of the mixture, that is, without interposing any manufacturing step after the coating of the mixture, in order to prevent the polyether amide resin film from being exfoliated by the internal stress of the polyether amide resin film during the process for manufacturing an ink jet recording head. In other words, polyether amide film must be formed in the condition in which the coated mixture of the polyether amide resin and solvent can be heated at the above described temperature level.

Polymethyl-isopropenyl-ketone can be listed as one of the resins as the material for the liquid path mold which can be dissolved away when the ink jet recording head is formed with the use of the method disclosed in aforementioned Japanese Laid-open Patent Application 6-286149. The greater the amount, by which the temperature at which this resin is heated, is higher than 120°C, the harder it becomes for this resin to be dissolved away. Thus, the mixture of

polyether amide and solvent is desired to be coated on the protective film and heated, when this resin as the material for the liquid path mold is not on the substrate.

On the other hand, the aforementioned Japanese Laid-open Patent Application 11-11-348290 discloses an ink jet recording head manufacturing method in which polyether amide is used as the sealing layer between the substrate and liquid path walls. In this case, polyether amide resin is continuously coated on both surfaces of the substrate; more specifically, it is coated on the primary surface (top surface in drawing) of the substrate in order to form the sealing layer, and on the reverse surface (bottom surface in drawing) to form the mask layer for forming the liquid (ink) supply hole. Therefore, the accidental coating of the areas of the surface of the substrate other than the intended areas of the surface does not become fatal, improving thereby yield. Further, both surfaces of the substrate can be heated at the same time to reduce the internal stress of the polyether amide film. Further, after the formation of the etchant-resistant film on the polyether amide films on both surfaces of the substrate by patterning, the polyether amid films on both surfaces of the substrate can be etched at the same time, making it possible to reduce manufacturing cost. Thus, in the

present invention, the polyether amid film is formed before the formation of liquid path mold of the dissolvable material by patterning.

Figure 1(c) shows a step (d) in which the hole corresponding to the liquid (ink) supply hole is formed in the silicon oxide film by etching, with the polyether amide film 104 having the hole corresponding to the liquid (ink) supply hole used as the etching mask.

Figure 1(d) shows a step (e) in which the ink supply hole 106 is formed by anisotropically etching the substrate through the hole of the silicon oxide film. When forming the ink supply hole through the substrate, the substrate is desired to be anisotropically etched for the following reasons. That is, the rate at which an anisotropic crystalline substance is etched varies depending on the direction in which the substance is etched, relative to the crystal orientation axes. In other words, the relationship between the rate at which an anisotropic crystalline substance is etched in one direction and that in another direction is constant. Therefore, the depth of a hole formed by etching through the substrate can be geometrically controlled by controlling the width of the hole, on the side from which the etching of the hole is started, in consideration of the thickness of the substrate and

the width of the hole on the side from which the etching is started. The width of the hole at the reverse surface of the substrate from which the etching is started (longest distance across the hole) is to be chosen in consideration of the properties of an ink jet recording head to be manufactured, thickness of the substrate, etc.

The completion of the formation of the hole by the anisotropic etching, or the etching method in which etching progresses in the width direction as well as the depth direction, leaves the edge portion of the hole of the silicon oxide film as an etchant-resistant film projecting into the hole in the substrate as shown in Figure 1(d).

Figure 1(e) shows a step (f) in which the above described edge portion of the silicon oxide film projecting into the hole. The polyether amide film as an etchant-resistant film remains on the surface of the silicon oxide film without exfoliating or floating from the surface, during the above described step (d), etching step (e), and etching step (f). Thus, the etching fluid is allowed to contact only the tip 105 of the projecting edge portion of the silicon oxide film. Therefore, even if the length of time the substrate is kept dipped in the etching liquid is slightly increased to assure that the projecting edge portion of the silicon oxide film will be completely

removed, the effect of the etching liquid upon the portion of the silicon oxide film, which is desired to be left as a protective film, is negligible. Therefore, the protective film remains precisely covered with the polyether amide film, makes it easier to control the manufacturing process. Removing the projecting edge portion of the silicon oxide film as described above prevents the problem that the projecting edge portion of the silicon oxide film breaks into debris during the ink jet recording head manufacturing steps following the formation of the hole, for example, an assembling process, a packaging process, etc., or while an ink jet recording head is used.

Figure 1(f) shows the substrate after the polyether amide resin layer 104 as an etchant-resistant film has been removed in step (g). Through the above described steps, it is possible to yield an ink jet recording head substrate, the edge of the ink supply hole of which, on the reverse side, has no overhanging protective film, and the reverse surface of which is flawlessly covered with the silicon oxide film uniform in thickness.

Thereafter, in order to complete an ink jet recording head, the nozzle formation members such as the liquid path walls, orifice plate, etc., are formed on the primary surface of the substrate, and then,

ejection orifices are formed so that they correspond to the energy generation elements. More specifically, as has been well known, first, the liquid path layer having a predetermined shape is formed by pattering, on the primary surface of the substrate, of dissolvable resin. Then, the nozzle layer is formed on the liquid path layer, of photosensitive resin such as photosensitive epoxy resin, photosensitive acrylic resin, etc. Then, the portions of the photosensitive nozzle formation layer, other than the portions to be turned into the ejection orifices which will be connected to the liquid paths, are hardened by exposing them to light, creating the orifice plate. Then, the dissolvable resin layer is dissolved away, leaving thereby holes as liquid paths. These steps for forming the ejection orifices and liquid paths on the primary side of the substrate may be carried out all at once after the above described step (g), or before any one of these steps. Further, they may be separately carried out prior to one or more of these steps. In these steps, the primary side of the substrate is to be covered with protective agent to protect the primary side from the process for etching the substrate from the reverse side.

The following are the supplements to the description of the manufacturing steps described above:

As the method for etching the silicon oxide film, or removing the projecting edge portion thereof, in at least one step among the steps (b), (d), and (f), one of the known wet etching methods is suitable. A wet etching method which uses alkaline liquid can quickly remove the silicon oxide film. However, a wet etching method which uses hydrofluoric acid, or mixture of hydrofluoric acid and ammonium fluoride is preferable.

If polyether amide is used as the material for forming the etchant-resistant film in at least one of the steps (c) and (g), a chemical dry etching method is preferable as the method for removing the etchant-resistant film. As the gas to be used for such an etching method, mixed gas, at least one of the main ingredients of which is oxygen or tetrafluorocarbon, is desired.

As the etching fluid to be used for anisotropically wet etching the substrate in step (e), at least one in the group of hydrazine, water solution of KOH, water solution of TMAH (tetramethyl ammonium hydroxide), and EPW (ethylenediamine-pyrocatechol-water) is desired. Such etching liquids are effective for anisotropic etching. When using only the water solution of TMAH as the etching liquid, the concentration thereof is desired to be no less than 15% and no more than 30%, in mass. The etching

temperature is desired to be in the range of 70°C - 90°C. When these conditions are satisfied, etching creates a hole with a smooth surface (111). Creating a hole with smooth surfaces, as the ink supply hole, is desirable because the amount by which the substrate dissolve into ink from the smooth surface thereof when alkaline ink is used, is substantially smaller than the amount by which the substrate will dissolve into ink from the rough surface of thereof when alkaline ink is used.

When an ink jet recording head substrate is manufactured through the above described steps, the problem that the silicon oxide film used as the etchant-resistant film for forming the ink supply hole is left projecting into the ink supply hole does not occur. Therefore, when this substrate having no silicon oxide film projection which might turn into debris is used for manufacturing an ink jet recording head, it is possible to manufacture an ink jet recording apparatus, which is excellent in ink ejection properties, being therefore capable of forming a high quality image.

Next, an ink jet recording head manufacturing process in which the silicon oxide film as a protective film is not etched will be described as a comparative example of an ink jet recording head manufacturing process, with reference to Figure 3.

Figure 3(a) shows a silicon substrate 301, on which a silicon oxide film 303 is formed, across the reverse surface thereof, that is, the surface on which energy generation element 302 are not present.

Figure 3(b) shows the silicon substrate 301 after a polyether amid film 304 as an etchant-resistant film was formed on the silicon oxide film, the surface of which had not been etched, and the hole for forming an ink supply hole was formed through the polyether amide film 304 by patterning.

Figure 3(c) shows the silicon substrate 301 after the hole for forming the ink supply hole was formed through the silicon oxide film, and the ink supply hole 306 was formed by anisotropic etching, leaving the edge portion 305 of the combination of the silicon oxide film and polyether amide film projecting into the ink supply hole 306, as a result of the progression of the anisotropic etching in the direction parallel to the surfaces of the substrate 301.

Figure 3(d) shows the silicon substrate 301, the silicon oxide film on which was removed from the wide area of the reverse surface of the substrate 301 surrounding the ink supply hole 306, by the etching liquid used for removing the portion 305 of the silicon oxide film projecting into the ink supply hole 306, because the polyether amide film exfoliated from

the silicon oxide film, from the area of the silicon oxide film around the ink supply hole 306, and the etching liquid entered between the polyether amide film and silicon oxide film.

Figure 3(e) shows the silicon substrate 301 having a step 307 which resulted because of the removal of the unintended portion of the projecting portion of the silicon oxide film, that is, the portion of the silicon oxide film other than the portion projecting into the ink supply hole 306. This step 307 allows the water used during a dicing process, to seep, while carrying debris therewith, into unintended areas, along the step 307, creating problems. Further, the removal of the silicon oxide film exposes the substrate surface, the crystallographic plane of which is not (111), although it depends on the condition under which the silicon substrate was manufactured. For example, a wafer, the crystal orientation plane of which is (100), is used as the substrate, the surface parallel to the crystallographic plane (100) is exposed. If an ink jet recording head substrate in this condition is pasted to a chip plate for forming the ejection orifices and liquid paths, to manufacture an ink jet recording head, ink will come into contact with the portion of the substrate not coated with silicon oxide film, although it depends on the level of accuracy

with which the substrate is pasted to the chip plate. This surface is less resistant to alkaline liquid compared to the surface, parallel to the crystallographic plane (111), of the ink supply hole of the substrate formed by anisotropic etching. Thus, if a substantial number of areas of the internal surfaces of the ink supply hole and ink paths of an ink jet recording head, which come into contact with ink, are parallel to the crystallographic plane (100), the amount by which silicon will dissolve into ink is not negligible, making it possible for the ink jet recording apparatus to be reduced in quality, in consideration of the fact that such ink that contains alkaline solution may be used.

Embodiment

(Embodiment 1)

Figure 2 shows the ink jet recording head manufacturing steps in the first embodiment of the present invention.

As the substrate, a 625 µm thick silicon wafer, which is formed of a silicon crystal, the crystallographic plane of which is (100), and the surfaces of which are parallel to the crystallographic plane of the silicon crystal, was used. In this embodiment, a large number of ink jet recording head substrates shown in Figure 2 are formed on each of five pieces of the aforementioned silicon wafer, using

the general purpose semiconductor manufacturing process. On the primary surface (top surface in drawing) of each substrate, heat generating resistor 211 as energy generation elements, driving circuits therefor (unshown), and electrodes for externally supplying the heat generating resistors 211 and driving circuits therefor with signals and electric power, had been formed. On the surface of the substrate, opposite to the surface having the heat generating resistors 211, that is, the reverse surface (bottom surface in drawing), a 700 nm thick silicon oxide film 212 as a protective film was present, which was formed by steam oxidization method during the formation of the insulating separation film, in the MOS formation process (Figure 2(a)).

The surface of the substrate on which the heat generating resistors and driving circuits therefor had been formed was coated, for protection, with positive resist (OFPR-800 (commercial name: Tokyo Oka Co.) to a thickness of 7 µm. The portions of the substrate, which create problems if they come into contact with etching liquid, should be prevented from coming into contact with etching liquid, with the use of a jig comprising an O-ring, rubber resist, or the like.

The five wafers, across which a large number of the above described ink jet recording head

substrates had been formed, were placed in an automatic etching bath comprising an wafer shaking mechanism, as shown in Figure 6. The bath was filled with mixture of hydrofluoric acid with a concentration of 16% in mass and hydrofluoric ammonium with a concentration of 27% in mass. The wafers were left in the bath for four minutes at the room temperature, to clean the surface of the silicon oxide film by etching it. Then, they were thoroughly cleaned with water, and then, dried. The etching fluid used for this process is desired to contain hydrofluoric acid. The concentration thereof does not need to be limited to the above described one. Further, the etching fluid may contain surfactant or the like, which has cleaning effects.

After the separation of the positive resist (Figure 2(b)), both the primary and reverse surfaces of the substrate (wafer) were coated with polyether amid resin, with the use of a spin coating apparatus. Then, the substrate (wafer) was baked at 250°C, forming thereby think film of polyether amide on both surfaces. Then, both surfaces were coated with positive resist to a thickness of 7 μm for the second time. Next, the positive resist layer on the primary surface, or the surface with the heat generating elements and driving circuits therefor, was patterned with the use of photolithographic technologies to

leave the positive resist across the areas in which the polyether amide is to be left as a sealing layer.

On the other hand, the positive resist on the reverse surface of the substrate was patterned so that the polyether amide film as an etching resistant film will be patterned as the mask for forming the ink supplying hole. Next, the polyether amide films on both the primary and reverse side of the substrate were patterned at the same time by chemical dry etching which used the mixture of CF_4 and O_2 gases.

Next, polymethyl-isopropenyl-ketone 213, that is, the liquid path formation material which could be dissolved away in the later process, was coated, and patterned (exposed to UV rays and developed). Then, it was coated with cationic polymerization epoxy resin 214, and then, was developed, yielding thereby a nozzle plate having a plurality of liquid ejection orifices.

Next, cyclized rubber 215 was coated on the primary surface and the adjacencies thereof to a thickness of 50 μ, in order to protect the nozzle plate on the primary surface of the substrate. Then, the substrate (wafer) was baked at 100°C.

Then, the wafers on which the plurality of unfinished ink jet recording head had been formed was placed in the above described automatic processing bath, containing the mixture of hydrofluoric acid and

ammonium fluoride as it previously did, and was kept therein for eight minutes at the room temperature, in order to etch the silicon oxide film.

Next, the wafers (substrates) were thoroughly washed with water, and dried. Then, they were dipped in water solution (21 wt.%) of TMAH (tetramethyl ammonium hydroxide) having a temperature of 83°C, and kept therein for 16 hours to allow the wafers (substrates) to be anisotropically etched to form the ink supply holes (Figure 2(c)).

Next, the substrates (wafers) through which the ink supply holes had been formed was dipped in the mixture of hydrofluoric acid and ammonium fluoride similar to the above described mixture, and kept therein for 12 minutes to remove the portions of the silicon oxide film, which had been left projecting into the ink supplying holes as the anisotropic etching progressed in the direction perpendicular to the thickness of the substrates (Figure 2(d)).

Thereafter, the polyether amide film was removed by the chemical dry etching which used the mixture of CF_4 and O_2 gases. After the removal of the polyether amide film, the width of the opening of the ink supply hole on the reverse side of the ink jet recording head substrate was 1,000 µm, and that on the primary side was 130 µm.

Thereafter, the cyclized rubber 215 on the

primary surface and its adjacencies was removed with xylene. Then, the entirety of the polymethyl-isopropenyl-ketone layer 213 as the liquid path formation material on the primary side of the substrate was exposed to UV rays. Then, the substrates (wafers) were dipped into methyl lactate, dissolving away the liquid path formation material (Figure 2(e)).

Lastly, the wafers were diced by a dicer to separate the plurality of the ink jet recording head.

(Comparative Process 1)

The comparative ink jet recording head manufacturing process is an example in which the silicon oxide film as the protective film was not etched.

Five wafers, across the surfaces of which 4700 Å thick silicon oxide film had been formed to make the silicon oxide film uniform in thickness after the cleaning-by-etching step in the first embodiment, were prepared. Otherwise, that is, except that the surface of the silicon oxide film was not etched for cleaning, this process was the same as the process in the first embodiment. Using this process, ink jet recording heads were manufactured under the same conditions as those in the first embodiment.

The ink jet recording heads manufactured using the ink jet recording head manufacturing

processes in the first embodiment and the comparative process were examined in terms of the condition of the silicon film on the reverse surface of the substrate, and also, were subjected to printing tests.

(Surface Examination)

The reverse surfaces of the ink jet recording heads were examined with the use of a metallurgical microscope. The results are given in Table 1. In the table, "wafer position in bath" means the position of the wafer in the automatic etching bath, shown in Figure 6, having a wafer shaking mechanism, relative to the bath.

TABLE 1

CONDITION OF SILICON OXIDE FILM IN ADJACENCEIS OF INK SUPPLY HOLE

WAFER POS. IN BATH	NEAR EDGE	NEAR EDGE	NEAR EDGE	NOT NEAR EDGE	NOT NEAR EDGE	NOT NEAR EDGE
HEAD POS. IN WAFER	OUTER-MOST	NEAR EDGE	CENTRAL	OUTER-MOST	NEAR EDGE	CENTRAL
EMB. 1	G	G	G	G	G	G
COMP. 1	NG	NG	G	NG	G	G

Figure 4 is a photographic of the reverse side of a typical ink jet recording head evaluated as G in Table 1, and Figure 5 is a photographic of the reverse side of a typical ink jet recording head evaluated as NG in Table 1.. In the case of an ink jet recording head having the evaluation mark of G, the silicon oxide film 402 remains on the reverse surface of the substrate in such a condition that it uniformly covers the surface of the substrate to the very edge of the ink supply hole 401 as shown in Figure 4. In comparison, in the case of the ink jet recording head evaluated as NG in Table 1, the silicon oxide film has been removed from the adjacencies 503 of the ink supply hole 501, creating thereby a step 504 between the surface portion covered with the silicon oxide film and the surface portion having no silicon oxide film. Thus, such a problem that the substrate (formed of silicon) dissolves into ink from the adjacencies of the ink supply hole, which are not covered with the silicon oxide film, might occur.

As will be evident from Table 1, in the case of the comparative ink jet recording head manufacturing process 1, the ink jet recording heads given the evaluation of NG were from the peripheral and near-peripheral portions of the wafer which was closer to the end portions of the bath, in terms of the direction perpendicular to the wafers (substrates).

Further, the ink jet recording heads from the peripheral portion of the wafer which was in the center portion of the bath were also given the evaluation of NG. This occurred for the following reasons. That is, one of the surfaces of the wafer(s) at the end(s), in terms of the direction perpendicular to the wafers, was not covered with another wafer, being thereby constantly supplied with a fresh supply of the mixture of the hydrofluoric acid and ammonium fluoride solutions. Therefore, the rate at which these wafers was increased, causing thereby the polyether amide film as the etching resistant film to float from the silicon oxide film. Further, regarding each wafer, the closer to the periphery of the wafer the given area of the wafer, the greater the amount by which the mixture of the hydrofluoric acid solution and ammonium fluoride solution is supplied thereto, and therefore, a phenomenon similar to that which occurred to the end wafer, occurred to the peripheral area of the wafers in the center portion of the bath. In this embodiment, the wafers were shook in the automatic etching bath. The occurrences and extent of these phenomena can be controlled to a certain degree by the provision or non-provision of the shaking, or improving the manner in which the wafers are shaken. In addition, it is possible to devise the automatic etching bath in structure; for example, providing the

bath with a liquid circulating mechanism, or eliminating it therefrom, changing the positions of the inlet and/or outlet of the etching liquid, etc. However, it is virtually impossible to absolutely uniformly expose to the etching liquid, all the surfaces of all the wafers in the automatic etching bath.

In comparison, in the case of the first embodiment, even when the etching process nonuniformly progressed, the polyether amide film did not float from the surface of the substrate of any of the ink jet recording heads, because the level of adhesion between the polyether amide film as the protective film, that is, the etchant-resistant film, and the silicon oxide film was substantially higher. As a result, all the ink jet recording heads manufactured with the use of the ink jet recording head manufacturing process in the first embodiment received the evaluation of G.

(Printing Tests)

The ink jet recording heads manufactured with the use of the ink jet recording head manufacturing processes in the first embodiment and the comparative process 1 were kept in a storage, being left unattended, for one month. Then, they were mounted in an ink jet printer (BJ-F900 (commercial name): Canon Inc.), and were subjected to printing tests, in which

the images formed by these ink jet recording heads were examined with naked eyes. Those which produced excellent images were given the evaluation of G, whereas those which produced images with a certain amount of anomalies were given the evaluation of NG. The results are given in Table 2.

TABLE 2

EVALUATIONS OF

INK JET RECORDING HEADS IN PRINT QUALITY

WAFER POS. IN BATH	NEAR EDGE	NEAR EDGE	NEAR EDGE	NOT NEAR EDGE	NOT NEAR EDGE	NOT NEAR EDGE
HEAD POS. IN WAFER	OUTER-MOST	NEAR EDGE	CENTRAL	OUTER-MOST	NEAR EDGE	CENTRAL
EMB. 1	G	G	G	G	G	G
COMP. 1	NG	NG	G	NG	G	G

It is evident from Table 2 that some of the ink jet recording heads manufactured with the use of the comparative process 1 were evaluated as NG in terms of image quality, whereas those manufactured with the use of the process in the first embodiment were all evaluated as G, that is, being excellent in image quality. In other words, the usage of the ink

jet recording head manufacturing process in accordance with the present invention makes it possible to increase the yield of an ink jet recording head of excellent quality, making it thereby possible to reduce ink jet recording head cost.

While the invention has been described with reference to the structures disclosed herein, it is not confined to the details set forth, and this application is intended to cover such modifications or changes as may come within the purposes of the improvements or the scope of the following claims.